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Effects of Current Density, Electrolyte Agitation, and Electrolyte Concentration on Copper Electrorefining in Nitrate Solution

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Abstract *– Copper applications in the 21st century demand high-performance properties, requiring fewer impurities in copper metal. Consequently, purification methods such as electrorefining have been studied. Electrorefining uses electricity to achieve high-purity copper, but traditional copper sulfate baths face challenges due to the presence of sulfur. This research explores copper electrorefining using nitrate solution, an alternative approach in the industry. The study investigates factors influencing copper purity, such as electrolyte agitation, copper concentration, and current density. Three levels of current density (50, 100, and 150 A/m²) and Cu concentration (20, 40, and 80 g/L) were tested, with and without agitation, at room temperature and constant agitation flow rate. ANOVA revealed that agitation and copper concentration significantly influence copper purity ($p = 0.04$ and $p = 0.006$, respectively), while current density is insignificant ($p = 0.052$), at 95% confidence level. Agitation generally improves current efficiency, whereas side reactions and dendrite formation are detrimental. The best conditions for electrorefining are Cu concentration of 40 g/L and current density of 100 A/m² under agitated conditions, which is validated by confirmatory testing. This study highlights the potential of nitrate solutions for copper electrorefining and suggests further investigation into temperature, agitation rate, electrode geometry, and addressing issues like surface morphology and corrosion to improve both purity and current efficiency.*

Keywords*: Electrorefining, Electrometallurgy, copper, copper nitrate*

I. INTRODUCTION

Copper is widely regarded as one of the most important industrial metals due to its mechanical properties, including high ductility, malleability, and excellent thermal and electrical conductivity. Prior to its application in the manufacture of pipes, electrical wiring, and motor components, copper-bearing ores must undergo a series of processing steps that vary depending on the ore type. For sulfidic ores, the conventional processing route involves mining, comminution, concentration, smelting, conversion, and electrorefining [1]. In traditional electrorefining, impure copper anodes—typically containing 98.5% to 99.5% copper—are electrochemically dissolved in an aqueous electrolyte consisting of copper sulfate and sulfuric acid [2]. In electrorefining, copper ions (Cu^{2+}) generated at the anode migrate through the electrolyte to the cathode, where they are reduced to high-purity metallic copper. Ideally, only copper is deposited at the cathode; however, certain impurity elements with similar standard reduction potentials or strong interactions with copper may co-deposit, thereby affecting the purity of the copper. The copper produced via conventional electrorefining typically achieves a purity of ~99.95%, which is sufficient for most industrial applications. However, the production of ultra-high purity copper (UHPC), defined as copper with a purity greater than 99.999%, is critical for expanding its use in advanced technologies such as semiconductor and microelectronic devices, high-performance audio components, and precision instrumentation [3]. A key limitation in achieving UHPC is the presence of sulfur-based impurities originating from the copper sulfate electrolyte. Sulfur exhibits a high affinity for copper and is often retained as a residual impurity in the refined metal [4-5]. To address this issue, alternative electrolytes have been investigated. Copper nitrate has emerged as a potential substitute due to its comparable conductivity. Preliminary studies have demonstrated that electrorefining in copper nitrate media can produce UHPC [1], [5-6]; however, several critical research gaps remain unaddressed in the existing literature. Neither study employed statistical analysis to evaluate the significance and relative influence of key process parameters, such as current density, copper concentration, and electrolyte agitation, on copper purity optimization. The reported findings were primarily based on single trials or limited replication, making it difficult to distinguish actual process effects from experimental variability. Although optimal operating conditions were proposed, these parameters were neither systematically optimized using design-of-experiments approaches nor validated through independent confirmatory experiments. Furthermore, although Choi and Kim (2003) utilized electrolyte circulation during electrorefining, agitation was not investigated as an independent experimental variable [5]. In contrast, Kekki et al. (2015) conducted all experiments under non-agitated conditions [6]. Consequently, the influence of electrolyte agitation on copper purity and current efficiency remains insufficiently understood. The present study addresses these gaps by systematically evaluating the effects of key operating parameters through statistical analysis, thereby providing a stronger basis for future studies related to ultra-high purity copper (UHPC) production.

This study investigates the effects of key electrorefining parameters—specifically current density, electrolyte agitation, and electrolyte concentration—on the purity of copper obtained through electrorefining in a copper nitrate solution, establishing a basis for future research related to UHPC production. The effects of these parameters are evaluated using Analysis of Variance (ANOVA), while the best operating conditions are identified using Taguchi analysis. A full factorial experimental design is employed, comprising a 2^1 and 3^2 structure: three levels are assigned to current density and electrolyte concentration, while two levels (presence or absence) are assigned to electrolyte agitation. Due to material constraints, the copper nitrate electrolyte solution was synthesized in-house at the Extractive Metallurgy Laboratory of the Department of Mining, Metallurgical, and Materials Engineering (DMMME). Elemental analysis of both the refined copper and the electrolyte solution was conducted using X-ray fluorescence (XRF) analysis. Moreover, stainless steel is selected as the cathode material for all experiments, offering a more economical alternative to titanium while maintaining adequate performance under the test conditions.

II. METHODOLOGY

In this study, the electrolyte used was synthesized copper nitrate, produced by dissolving copper plates in nitric acid. Before electrorefining, the synthesized electrolyte was heated and subsequently filtered through filter paper to eliminate slimes and other impurities. Presented below are the chemical reaction for the synthesis (Eq. 1) and the elemental impurity profile of the electrolyte Table 1 as measured using XRF. The XRF instrument used in this study had a detection limit ranging from 1 ppm to 100% elemental concentration.

$$Cu_{(s)} + 4HNO_{3(aq)} \rightarrow Cu(NO_3)_{2(aq)} + 2NO_{2(g)} + 2H_2O_l \tag{1}$$

Table 1. Elemental impurity profile of synthesized copper nitrate

Element	Concentration /ppm	Uncertainty /ppm
Cr 24	6.9	± 3.1
Cu 29	96949	± 440
Fe 26	67.5	± 10.6
Sr 38	1.7	± 0.7

Copper plates used as anodes were also analyzed using XRF to determine anode purity. Multiple analyses were conducted at different locations on each copper plate to obtain a more accurate measurement. Nitric acid was used to adjust the solution pH to 1.4 – 1.7. Copper and stainless steel electrode sheets were cut to dimensions of 8 x 6 cm^2 with a thickness of 1.2 mm and polished using 1000-grit SiC paper to remove oxide layers. After preparation, the electrodes were immersed in a 450 mL electrolyte contained in a modified 600-mL beaker, with an effective deposition area of 32.4 cm^2 (5.4 cm x 6 cm). A voltage of 3.0 V was set before electrorefining, while current was maintained depending on the predetermined current density values for each run. For setups with agitation, an electrorefining cell equipped with a pump-driven agitation system was used, as shown in Figure 1. The pump was connected to the cell via tubing, maintaining a flow rate of 100 mL/min.

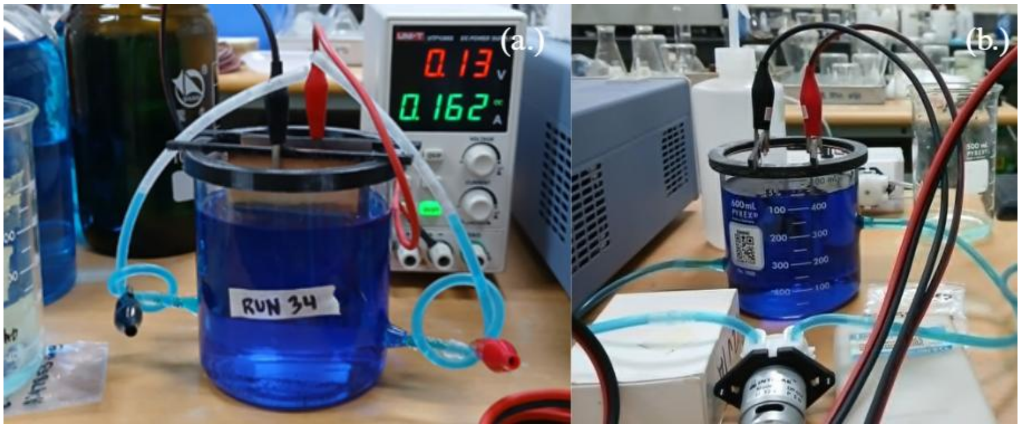

Figure 1. Electrorefining setup (a.) without and (b.) with agitation

After electrorefining, the deposited copper was stripped from the cathode and analyzed using XRF analysis. Following data collection, statistical analysis was performed. The significance of each factor was evaluated by comparing its p-value against an alpha level of 0.05.

In this study, electrorefining parameters such as pH, cathode-to-anode distance, temperature, and time were kept constant. Table 2 summarizes these constant parameters. The pH was maintained between 1.4 and 1.7 to prevent cet.etorrosion of copper and the reduction of nitrate ions [5-7]. The cathode-to-anode distance was set at 2 cm. Moreover, electrorefining was carried out at room temperature, as it was observed that copper purity decreased when the temperature exceeded room temperature during electrorefining in a nitrate solution [5-6]. Existing studies show that copper purity and quality improve at sufficiently low copper concentrations and current densities. A study conducted by Kekki et al. in 2014 achieved the optimum purity of copper using a 40 g/L Cu concentration and 100 A/m² current density, while Choi and Kim achieved a purity of 6N using approximately 47 g/L Cu concentration and 100 A/m² current density by employing waste copper nitrate for the electrorefining of copper [5-6]. In this study, even lower values of both parameters were tested to see if they would further improve the process. Process duration was set to 4 hours for medium and high current densities, and 6 to 12 hours for low current density; this is to have at least 1 gram of deposited copper at the cathode.

Table 2. Constant parameters

Parameter	Value	Unit
pH	1.4 – 1.7	
Cathode to anode distance	2	cm
Time	4 to 12	Hours
Temperature	< 35	°C

The experiment followed a 2^1 and 3^2 full factorial design, with two (2) replicates for each treatment combination. Current densities of 150, 100, and 50 A/m^2 were tested, along with electrolyte concentrations of 80, 40 and 20 g/L. To assess the effect of electrolyte agitation on the electrorefining of copper in nitrate solutions, experimental setups were constructed both with and without agitation system.

III. RESULTS AND DISCUSSION

Table 3 presents the copper purity and corresponding current efficiency for each experimental run. All purity values exceeded that of the anode (99.81%, as measured by XRF), indicating an increase in purity. The highest copper purity achieved was 99.9038% (Run 5), obtained under agitated conditions with a copper concentration of 40 g/L and a current density of 100 A/m². In contrast, the lowest purity of 99.8416% (Run 16) was obtained without agitation at a copper concentration of 80 g/L and a current density of 50 A/m². As for the processes efficiency, Run 8 yielded the highest current efficiency (99.41%), while Run 6 produced the lowest (82.42%).

Notably, no direct correlation (-0.2791) was observed between copper purity and current efficiency. Runs exhibiting high current efficiency may still yield relatively low copper purity due to the co-deposition of impurities on the cathode.

Table 3. Copper purity and current efficiency at varying Cu concentration and current density with and without agitation

Run	Agitation	Cu Conc, g/L	Current Density, A/m^2	Ave Cu Purity, %	Ave Current Efficiency, %	SD (Purity)	SD (CE)
1	**with**	**20**	**50**	99.8707	94.8276	0.0121	0.0377
2	**with**	**20**	**100**	99.8759	89.2602	0.0148	0.9806
3	**with**	**20**	**150**	99.8719	94.7039	0.0128	0.1205
4	**with**	**40**	**50**	99.8756	96.2337	0.0198	0.1201
5	**with**	**40**	**100**	99.9038	95.9463	0.0146	0.0868
6	**with**	**40**	**150**	99.8863	82.4220	0.0127	0.9087
7	**with**	**80**	**50**	99.8666	97.5592	0.0168	1.1009
8	**with**	**80**	**100**	99.8596	99.4130	0.0092	0.4021
9	**with**	**80**	**150**	99.8552	98.5342	0.0138	0.7762
10	**without**	**20**	**50**	99.8569	92.7096	0.0157	0.9189
11	**without**	**20**	**100**	99.8703	89.0012	0.0119	0.9362
12	**without**	**20**	**150**	99.8722	91.0987	0.0035	0.2920
13	**without**	**40**	**50**	99.8667	93.3920	0.0117	0.5044
14	**without**	**40**	**100**	99.8791	92.9279	0.0188	0.9781
15	**without**	**40**	**150**	99.8631	88.8525	0.0189	0.9732
16	**without**	**80**	**50**	99.8416	93.7040	0.0274	0.9726
17	**without**	**80**	**100**	99.8709	92.6770	0.0096	0.8819
18	**without**	**80**	**150**	99.8616	97.4421	0.0169	0.6722

Agitation generally improved both purity and current efficiency, except at certain setups, as shown in Figure 2 and 3, likely due to improved mass transport and reduced concentration gradients within the electrolyte.

Under agitated conditions, the intermediate copper concentration (40 g/L) produced the highest purity, followed by the low (20 g/L) and high (80 g/L) settings. This trend can be attributed to several factors, including side reactions at the low concentration setting, as well as high ion availability and a relatively greater number of impurities at the high concentration setting. Given that the copper nitrate solution was synthesized using used copper anodes, the high concentration setting inherently contained more impurities, which can co-deposit on the cathode alongside copper. Furthermore, for both the low and intermediate concentration settings, the intermediate current density (100 A/m^2) yielded the highest purity. In contrast, at the high copper concentration, purity declined with increasing current density. The drop in purity at 150 A/m^2 may be attributed to the entrapment of impurities within dendritic structures, which form as a result of localized increases in current density at the cathode during deposition.

In contrast to the agitated setups, the effect of copper concentration was less pronounced without agitation, as the purity values showed little variation, particularly at intermediate and high current densities.

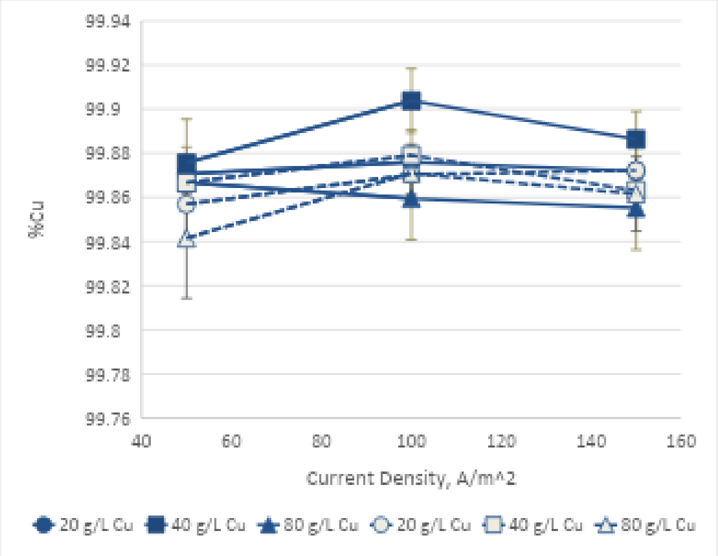

Figure 2. Copper purity vs. current density at varying copper concentrations with (solid lines) and without agitation (dashed lines)

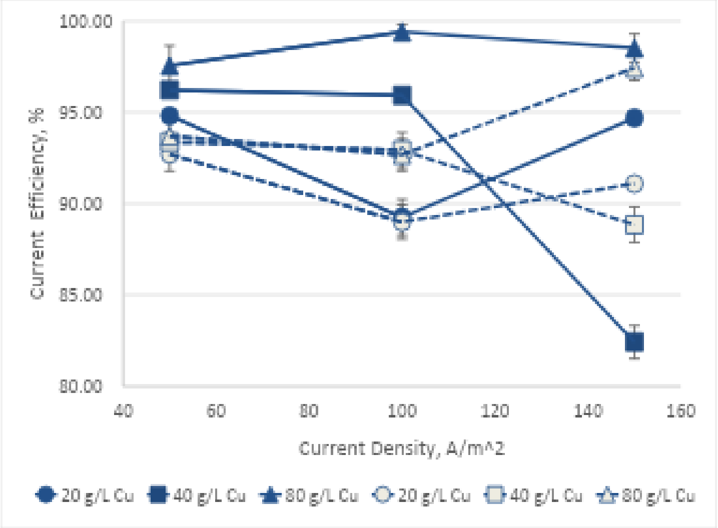

Figure 3. Current efficiency vs. current density at varying copper concentrations with (solid lines) and without agitation (dashed lines)

At low Cu concentration (20 g/L), ion availability in the solution is limited, causing side reactions to happen, including the evolution of gases at the cathode. A notable observation on the runs operated at low Cu concentration is uneven deposition of copper ions due to hydrogen gas evolution on the surface. Bubbles, which occupied some portions on the surface of the cathode, resulted in voids or areas deprived of copper, as shown in Figure 4. These side reactions competed with copper deposition, resulting in low current efficiencies. The hydrogen gas evolution more prevalent at low current density than at the intermediate current density. This is possibly because, when a low current density is applied, the cathode potential is insufficient to drive rapid copper deposition, causing electrons to reduce hydrogen and nitrate ions instead. At 100 A/m², the higher overpotential substantially increases the rate of Cu^{2+} reduction. It is not that side reactions are actively suppressed at higher overpotentials—their absolute rates may also increase—but rather that the relative contribution of copper deposition to the total current becomes larger.

The deposition was also accompanied by dendrite formation at the edges, especially at low and high current density settings, due to a localized increase in current density at the cathode. Dendrites are needle-like or tree-like structures that grow unevenly on the cathode during the electrorefining process under activation or mixed control [8-9]. These dendrites form when the deposition rate is faster at certain localized points due to excessive current density [10]. Dendrite formation is undesirable for the electrorefining process, as they can trap impurities from the electrolyte, such as iron and other trace metals [8], thereby decreasing the purity of copper. Electric current follows the path of least resistance. At the edges and corners of the cathode, the electric field lines converge and become more concentrated compared to the flat central surface. This results in a locally higher current density at the edges than the average current density applied to the entire electrode.

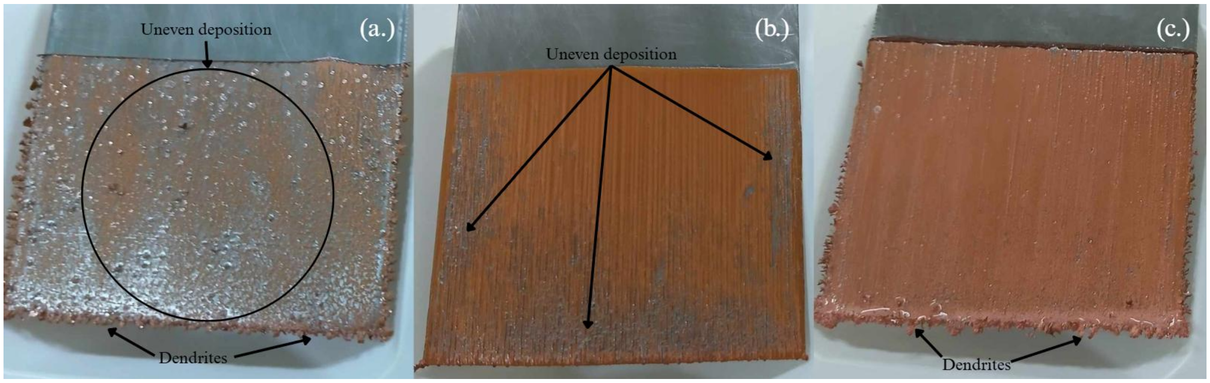

Figure 4. Electrorefining at 20 g/L Cu concentration at (a.) 50 A/m^2, (b.)100 A/m^2, (c.) 150 A/m^2

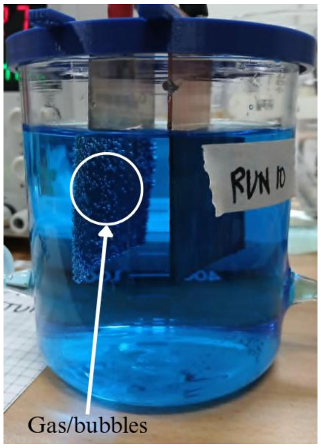

Figure 5. Electrorefining at 20 g/L Cu and 50 A/m^2

At 40 g/L Cu, adequate ion availability allowed uniform copper deposition across the cathode's surface without overwhelming the system with excess ions. At this concentration, there was no formation of dendrites at low and intermediate settings of current density. On the other hand, dendrites were formed on the surface and at the edges at high current density. This excessive dendrite formation resultetd in extremely low current efficiency, 82.4220% for setup with agitation and 88.8525% for setup without agitation.

Figure 6. Electrorefining at 40 g/L Cu concentration at (a.) 50 A/m^2, (b.)100 A/m^2, (c.) 150 A/m^2 without agitation

At high concentration of copper (80 g/L), current efficiencies improved, especially with agitation. However, copper purity values were relatively low compared to purity values obtained from the 40 g/L Cu setting, likely due to too much availability of ions in the solution and co-deposition of impurities at the cathode, especially since a higher electrolyte concentration contains more impurities. High copper concentration leads to excessive ion concentration in the solution, resulting in an increase in the overall ionic strength of the solution, as well as the viscosity and density of the solution, which can reduce the selectivity of the electrodeposition process or lower copper purity by affecting ion diffusivity and the movement of impurities [11].

At low current density and high copper concentration without agitation (Run 16), the electrorefining was accompanied by an increase in pH (2.4) and the formation of dark patterns on the cathode surface (indicative of corrosion), which resulted in relatively low current efficiency and the lowest purity (99.8416%). This behavior may indicate side reactions such as nitrate ion reduction. Nitrate ion reduction competes with copper deposition, thereby lowering the current efficiency and potentially introducing localized pH shifts near the electrode that destabilize deposition. When nitrate ions are reduced, species such as nitrite, nitrogen gas, and ammonia may be produced, which can react with copper ions or form surface deposits [12].

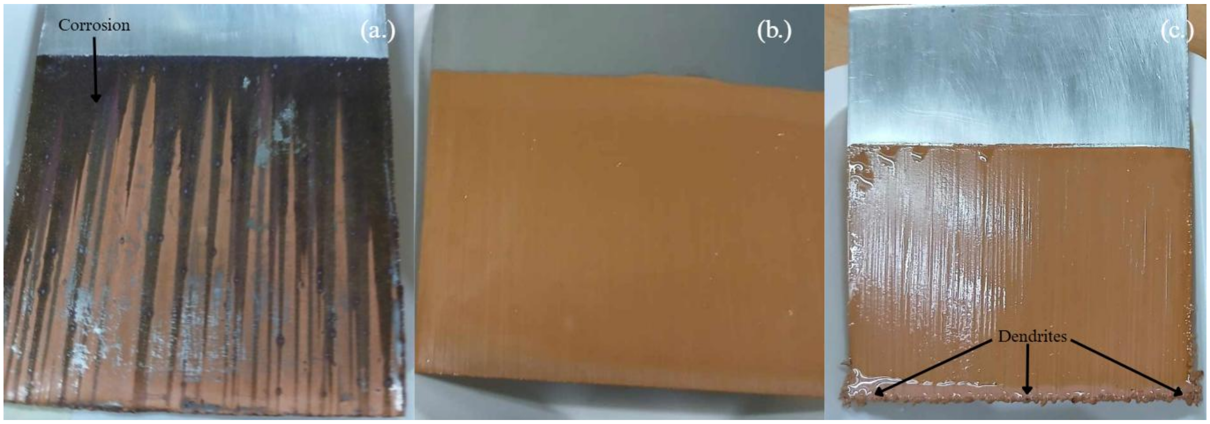

Figure 7. Copper deposition at 80 g/L Cu concentration at (a.) 50 A/m^2, (b.)100 A/m^2, (c.) 150 A/m^2 without agitation

Based on ANOVA at a 95% confidence level, electrolyte agitation and copper concentration significantly affect copper purity (p = 0.04 and p = 0.006, respectively), while current density is insignificant (p = 0.052). Among these factors, copper concentration has the most significant effect on copper purity.

Table 4. ANOVA results for the copper purity data

Source	**P-value**	
Agitation	0.04	Significant
Cu Concentration	0.006	Significant
Current Density	0.052	Insignificant

Table 5 shows the response table of means for Taguchi Analysis. Based on the table, the combination of parameters that would result in highest purity are with agitation, 40 g/L Cu concentration, and 100 A/m^2 current density. To confirm this, a confirmatory run was conducted. Additionally, the delta values, which represent the difference between the maximum and minimum purity for each parameter, highlight copper concentration as having the greatest impact, with a delta of 0.02%. In comparison, agitation and current density both show smaller deltas of 0.01%, suggesting their influence on copper purity is less significant. Furthermore, copper concentration may require optimization, as it has the most noticeable effect on purity.

Table 5. Signal settings on purity of copper (Taguchi Analysis)

Level	Agitation	Cu Concentration	Current Density
1	99.87	99.87	99.86
2	99.86	99.88	99.88
3		99.86	99.87
Delta	0.01	0.02	0.01
Signal Settings	**Circ_1 (With)**	**Conc_2 (40 g/L Cu)**	**CD_2 (100 A/m²)**

Table 6 presents the best process conditions and their corresponding predicted and actual copper purity values. The parameters include "with" circulation, 40 g/L copper concentration, and 100 A/m2 current density. These settings represent the best conditions identified using the Taguchi analysis. According to the table, the actual purity achieved was 99.8967%, which closely aligns with the predicted purity from the Taguchi design model, which is 99.891%.

Table 6. Final settings for confirmatory testing

Agitation	Cu Concentration, g/L	Current Density, A/m^2	Predicted Purity, %	Actual Purity, %
With	40	100	99.891	99.8967

In summary, copper deposition requires copper ions to reach the cathode and gain electrons. When the ion concentration in the electrolyte is limited to only 20 g/L, side reactions become more likely as copper ions near the cathode get used up quickly and are not replenished fast enough due to mass transfer limitation, where the electrode runs out of copper ions locally, and thus competing reaction such as hydrogen gas evolution take over as the electrons still need somewhere to go. However, at higher copper concentration, the electrolyte contains a greater number of ions and impurities, which can co-deposit alongside copper and lower copper purity. Agitation helps by enhancing ion transport to the cathode by reducing concentration gradient in the solution. Moreover, higher current densities provide a stronger driving force for ions in the solution to migrate to the cathode, yet both excessively low and high current densities compromise deposit quality. At low current density, particularly when copper ions are scarce in the electrolyte, the lower driving force for ions migration or mass transport favors side reactions such as hydrogen evolution. This lowers current efficiency and contaminates the deposit with gas bubbles, oxides, or hydroxides—thereby reducing chemical purity. At high current density, rapid ion depletion near the cathode promotes dendritic growth due to uneven electric field distribution. While this primarily affects morphology (producing rough, porous, or loosely attached structures), it indirectly harms purity by trapping electrolyte and impurities, and by shedding particles that may redissolve. Thus, gas evolution degrades copper purity and efficiency, whereas dendrite formation degrades purity and mechanical integrity. Both ultimately limit deposit quality, underscoring why the combination of parameters in Table 6—with agitation, sufficient copper concentration (40 g/L), and moderate current density (100 A/m²)—is the best conditions for copper electrorefining in nitrate solution.

IV. CONCLUSION AND RECOMMENDATIONS

This study investigates the factors influencing copper electrorefining in nitrate solution, with emphasis on electrolyte agitation, copper concentration, and current density. Based on the results, the following conclusions are drawn:

1. Electrolyte agitation significantly improves copper purity ($p = 0.04$, $\alpha = 0.05$) by enhancing mass transport and minimizing concentration gradients within the electrolyte.

2. Copper concentration exhibits the most significant effect on purity ($p = 0.006$, $\alpha = 0.05$). The intermediate concentration (40 g/L) provides optimal conditions for uniform copper deposition and minimizes impurity incorporation. In contrast, low concentration (20 g/L) leads to limited ion availability, promoting side reactions and uneven deposition, while high concentration (80 g/L) increases the likelihood of impurity co-deposition due to the high number of ions and impurity content.

3. Current density has an insignificant effect on copper purity ($p = 0.052$, $\alpha = 0.05$) but influences the morphology of the deposited copper. Higher current densities promote dendritic growth, which can trap impurities and reduce purity, whereas lower current densities favor competing side reactions under certain conditions.

4. Side reactions (i.e. hydrogen gas evolution and nitrate ion reduction) and dendrite formation are detrimental to the current efficiency of the electrorefining process.

5. Agitation improves current efficiency.

6. Based on Taguchi, the best parameters for copper electrorefining in nitrate solution are found to be with agitation, 100 A/m² current density, and 40 g/L Cu concentration.

Existing studies on copper electrorefining in nitrate solution are limited, as copper nitrate is not the conventional electrolyte. Nevertheless, this research validates its potential as an effective electrolyte. Although the purity values obtained are lower than those in previous studies (e.g., 6N purity), the results reveal important trends in optimal parameter ranges and side reactions affecting deposition and surface quality, providing valuable baseline insights for future optimization and UHPC production. Previous studies achieving 6N purity used more advanced setups and ICP-OES, a more sensitive technique than the one used here, which may account for the lower purity values observed. Future work should adopt more sophisticated analytical methods to improve accuracy. To further enhance purity, additional factors such as temperature, agitation rate, and cathode-to-anode distance should be explored. Moreover, since some deposits exhibited poor surface quality and corrosion, methods to improve copper morphology—such as additives or alternative electrode geometries—are strongly recommended. A multidimensional approach will deepen understanding of the electrorefining process and contribute to producing ultra-high purity copper for industrial applications.

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